Low-Heat Cement and the Control of Temperature in Mass Concrete.

THE need for controlling the temperature rise during the setting and hardening of large masses of concrete if serious cracking is to be avoided is well known, and much attention has been given to the problem. The extent of the trouble is emphasised by experience in this class of work. An example is a series of measurements of temperature rise in a large concrete monolith built in the United States three or four years ago. This monolith was 40 ft. long by 26 ft. high, and is part of a spillway 500 ft. long. Temperatures were recorded in the mass and just inside the wood shuttering. When the concrete was placed the air temperature was o deg. Fahr., and ordinary Portland cement was used. The temperatures recorded were as follows : Interior of the mass—At 2 days, 140 deg. Fahr. ; at 4 days, 142 deg. Fahr. ; at 8 days, 140 deg. Fahr. ; at 12 days, 137 deg. Fahr.; at 26 days, 104 deg. Fahr. At the face—2 days, 89 deg. Fahr. ; 4 days, 94 deg. Fahr. ; 8 days, 79 deg. Fahr. ; 12 days, 66 deg. Fahr. ; 26 days, 62 deg. Fahr. The shutters were stripped 26 days after placing the concrete.

This rise in temperature is due to the heat evolved by the cement during the hardening process, and in order to reduce this special cements, known as low-heat cements, have been made for some years which evolve less heat on hydration than normal cements.

It has been found, however, that the use of low-heat cements does not solve the problem, and that other means have to be used to keep down the temperature. The problem was dealt with by Mr. Clarence Rawhouser in a paper read before the American Concrete Institute recently, and published in the Journal of the Institute for February, 1945. The conclusions reached by the author were based on a great deal of experience in the construction of dams for the Bureau of Reclamation.

The factors that affect the temperature of concrete are, he said, those due to climatic conditions at the time of placing the concrete and during the early hardening period, the water content of the concrete, the proportion of cement, the type and fineness of cement, the character of the aggregate, the size and shape of the work, the provision or otherwise of joints, the thickness placed at one time and the period between each lift, the volume of the work, the time of removal of the shuttering, and so on.   Of these factors the use of low-heat cement certainly has some effect on the temperature rise of the concrete, but recent tests and experience have shown that the type of cement alone, without consideration of other factors, has little effect in controlling the total temperature reached and its rate of decline.   Measurements made on 5 ft. lifts of concrete two days after placing showed that the average temperature of concrete made with ordinary Portland cement had a temperature only 16 deg. Fahr. higher than similar concrete in which low-heat cement was used, and that the temperature difference was about the same seven days after placing.   This difference appears to be of small consequence compared with the temperature of 142 deg. Fahr. reached in the monolith referred to four days after the concrete was placed when the air temperature was o deg. Fahr.   Mr. Rawhouser suggests that generally the placing temperature has a much more important bearing on the temperature and rate of cooling, and the consequent cracking of the concrete, than any change that may be effected by altering the heat-generating properties of the cement, and a discussion of the other factors that enter into the problem leads to some suggestions for their control, which may be summarised as follows.

Changes in the water content of the concrete are of minor importance. Aggregates vary very much in their thermal characteristics, and this should be taken into consideration where a choice of aggregates is available ; for example, concrete made with quartzite aggregate has a diffusivity nearly twice as great as a concrete made with a basalt aggregate.   Estimates based on the thermal properties of concretes used in a large number of dams suggest that it would take more than twice as long for the concrete in one dam to cool than in the case of another structure in which the only difference was the nature of the coarse aggregate.   The modulus of elasticity and creep characteristics of the concrete are important factors in the formation of cracks.   Experience has shown that concrete with a low modulus of elasticity compared with its strength and a relatively high creep coefficient is much less liable to cracking than is a concrete with normal elasticity and creep characteristics.   The spacing between contraction joints should generally be less than 50 ft., and for very large sections joints should be formed in two directions.   The concrete reaches its maximum temperature two or three days after it is placed ; it is therefore desirable that the shuttering should be removed and cold-water curing started before this period ; it is recommended that the shutters should be stripped and curing started the day after placing in order to check the rise in temperature.   A method of artificial cooling of the concrete by circulating cold water through a pipe system embedded in the concrete is recommended.   This enables the cooling to start immediately the concrete is placed, and it also has the advantage that

the whole of the mass can be cooled uniformly. The method has been used in connection with six dams ranging in size from 175,000 cubic yards to nearly ten million cubic yards, and the cost has ranged between 13 and 55 cents per cubic yard. The rate of placing the concrete has a considerable effect on the temperature rise ; lifts of 5 ft. have been generally adopted, and it has been found that about one-third of the total heat developed by hydration of the cement may be dissipated from the top of the lift if five days are allowed to elapse before the next is placed. Excessive cooling of the top of a lift, however, is liable to cause cracks after 12 to 18 days, and it is recommended that only five to ten days should be allowed to elapse between successive 5 ft. lifts. An effective reduction in maximum temperature has been effected by the adoption of 2½ ft. lifts. It is desirable that in massive structures the concrete should be placed during periods of low temperature so long as it can be prevented from freezing.

The paper describes the system of artificial cooling adopted by the Bureau. It comprises a number of embedded coils in parallel, served by supply and return headers. The coils, of 1 in. outside diameter, are of thin-wall metal tubing about 800 ft. long, with expansion-type couplings. The tubing is placed on the top of each 5 ft. lift of concrete when it has hardened, and at horizontal spacings of between 2 ft. and 6 ft. The velocity of flow through the coils is not less than 2 ft. per second, and the water is either pumped through the coils or a gravity system is used.

An effective factor in temperature control is the amount and type of cement used. The temperature rise of the concrete due to the heat of hydration of the cement may be considered to vary directly as the cement content. Increasing the fineness of the cement increases the amount of heat developed at early ages by about the same percentage as the strength is increased. The type of cement plays an important role in the total amount and rate of temperature rise due to heat of hydration. The type of cement alone, without consideration of other factors, has a very small effect in controlling the total temperature decline from maximum to final temperature in a given concrete structure of massive proportions. The total excess heat is made up of two components, namely, the amount by which the placing temperature exceeds the final temperature, and that due to the heat of hydration of the cement. Usually the placing temperature has a much more important bearing on the temperature decline and consequent contraction of the concrete than any change that may be effected by varying the heat-generating characteristics of the cement. However, in structures of smaller dimensions, such as thin arch dams or the buttresses of multiple-arch dams wherein the rate of loss of heat equals or exceeds the rate of heat generation at relatively early ages, the average maximum temperature attained by the concrete might be reduced by as much as 10 to 15 deg. Fahr. by the use of low-heat cement compared with ordinary Portland cement. The most efficient use of low-heat cement is in conjunction with artificial cooling with closely spaced cooling pipes as already described. The slower rate of heat generation with low-heat cement permits the removal of heat almost as fast as it is developed, so that the temperature rise of the concrete midway between pipes spaced 2 ft. 8 in.

apart can be limited to 5 or 6 deg. Fahr. Pozzolanic material is sometimes added to Portland cement and the mixture used to produce concrete which has somewhat the same properties as similar concrete made with low-heat cement. The effectiveness of this type of cement depends upon the amount and type of pozzolanic material and the type of cement.

The development of a concrete highly resistant to cracking by the selection of materials producing favourable physical properties offers a possibility that has not been adequately explored. Factors that must be considered in determining the relative resistance of various concretes to temperature-induced cracking are the temperature change, thermal coefficient of contraction and expansion, modulus of elasticity, creep characteristics, and the tensile strength. These are recognised as important properties of concrete, but attention is usually concentrated on a single one of these factors rather than on the combined effect of all of them. For instance, low-heat cement was specially developed to reduce the cracking resulting from large relative temperature changes that accompany the use of ordinary Portland cement in massive structures. The advantage of low-heat cement compared with ordinary Portland cement was originally based on the comparison of their heat-generating characteristics. A later comparison, made in objecting to the consideration of heat-generating characteristics by themselves, was based upon the strength-heat ratio of the different concretes. When this ratio of two factors is considered, the conclusion may be reached that concrete containing ordinary Portland cement is more resistant to temperature cracking than concrete made with low-heat cement. Actual behaviour in structures does not verify this conclusion. The modulus of elasticity and creep characteristics play an important part on the cracking tendency of different concretes. This is indicated in the relative behaviour of two large straight gravity dams of similar size and comparable exposure conditions constructed within recent years under similar careful control of the construction operations. Very little cracking was experienced in the concrete of the Hiwassee dam, which had an abnormally low modulus of elasticity compared with its strength and a relatively high creep coefficient. The concrete of Norris dam, which had normal elastic and creep characteristics, was cracked quite extensively. At Hiwassee dam a great deal of attention was given to controlling the temperature of the concrete, with the result that it was apparently more favourable than at the Norris dam. However, the marked difference in crack development could not be accounted for by the differences in temperature conditions alone. To a considerable extent it must be attributed to favourable physical properties of the concrete obtaining at the time critical temperature changes were taking place.

Portland-Pozzolana Cement.

Some information is now available about the behaviour of the concrete in the Bonneville dam on the Columbia river, which was built six years ago. In selecting the cement for the work low-heat of hydration was given preference over high strength, and a modified cement to which 25 per cent. of calcined pozzolanic material had been added was used ; in the event it was found that there was no

loss of compressive strength.   It is reported that the condition of the surface of the superstructure is now the same as it was at the time of construction, except for some scaling on one of the bridges due to the use of salt in freezing weather. Severe attrition occurred at the bases of piers downstream of the gates, and repairs have been carried out every year.   These repairs have been made with a variety of different types of cement, and admixtures have been used with the object of hardening the concrete, but there has been little difference in the time required for the erosion of these concretes compared with the original concrete ; the conclusion has been reached that concrete is not a suitable material for use at the surface in these areas, and they have now been covered with $\frac{1}{2}$ in. steel plates.   Erosion has also occurred at places adjacent to the baffles on the deck, but it is not considered that concrete of any composition would withstand the severe conditions met with in such areas.   In some cases repairs have been made with ordinary Portland cement concrete, and these surfaces have already become roughened.   It is, however, thought that the ordinary Portland cement concrete withstands water flowing at high velocity better than concrete made with pozzolanic cement.

The average rise in temperature of the mass concrete when placed was about 35 deg. Fahr., and it is considered that the effectiveness of the pozzolana cement in reducing the temperature rise was satisfactory.   Some cracks appeared during the cooling period, and a small amount of leakage occurred through some of them. This leakage stopped after about a year and it is reported that, while evidences of the cracks still exist, they have all become completely sealed and are not objectionable.   There is some dampness on the walls of the inspection tunnels, but in every other way the interior of the mass concrete is considered to be entirely satisfactory.

The Mechanics of the Compound Grinding Mill.

ON page 25 of the March number of this Journal, Fig. 2 was inadvertently turned through an angle of 90 degrees.   The diagram shows the path of the balls in grinding mills as printed below.
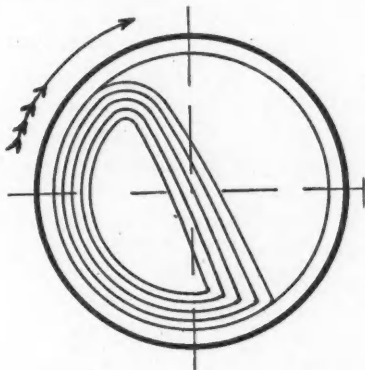
Hydrated Calcium Sulphoaluminates.

A DISCUSSION of the analogy of hydrated calcium silicoaluminates and hexa-calcium aluminate to hydrated calcium sulphoaluminates, by Mr. E. P. Flint and Mr. L. S. Wells, is presented in Research Paper No. 1,623 of the United States National Bureau of Standards. The following is an abstract of the paper.

The high-sulphate form of calcium sulphoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$, is a constituent of hydrated Portland cement and is also produced by the action of sulphate waters on concrete. Another compound, $3CaO.Al_2O_3.CaSO_4.12H_2O$, discovered by Lerch, Ashton, and Bogue, and known as the low-

TABLE I.—CALCIUM ALUMINATE COMPLEX SALTS THAT HAVE BEEN SYNTHETISED BY VARIOUS INVESTIGATORS.

TYPE I (1)	TYPE II (2)
$3CaO.Al_2O_3.3CaSO_4.31H_2O$	$3CaO.Al_2O_3.CaSO_4.12H_2O$
$3CaO.Al_2O_3.3CaCO_3.27H_2O$	$3CaO.Al_2O_3.CaCO_3.11H_2O$
$3CaO.Al_2O_3.3Ca(ClO_3)_2.30H_2O$	$3CaO.Al_2O_3.Ca(ClO_3)_2.10H_2O$
$3CaO.Al_2O_3.3Ca(CH_3CO_2)_2.30H_2O$	$3CaO.Al_2O_3.Ca(CH_3CO_2)_2.8H_2O$
$3CaO.Al_2O_3.3CaCrO_4.30H_2O$	
$3CaO.Al_2O_3.3CaSeO_4.30H_2O$	
$3CaO.Al_2O_3.3CaMnO_4.30H_2O$	
$3CaO.Al_2O_3.3Ca(IO_3)_2.30H_2O$	
$3CaO.Al_2O_3.3Ca(HCO_2)_2.30H_2O$	
$3CaO.Al_2O_3.3Ca(C_2H_5CO_2)_2.30H_2O$	
	$3CaO.Al_2O_3.CaCl_2.10H_2O$
	$3CaO.Al_2O_3.CaBr_2.10H_2O$
	$3CaO.Al_2O_3.CaJ_2.8H_2O$
	$3CaO.Al_2O_3.Ca(NO_3)_2.10H_2O$
	$3CaO.Al_2O_3.Ca(NO_2)_2.10H_2O$

(1) General Formula : $3CaO.Al_2O_3$ where $X.30\text{–}32H_2O$ or $3CaO\ Al_2O_3.3CaY_2.30\text{–}32H_2O$, where X is a bivalent, and Y a univalent acid radical.

(2) General formula : $3CaO.Al_2O_3.CaX.8\text{–}12H_2O$ or $3CaO.Al_2O_3.CaY_2.8\text{–}12H_2O$, where X is a bivalent, and Y a univalent acid radical.

sulphate form of calcium sulphoaluminate, has not been identified in hydrated Portland cement. Numerous other calcium aluminate complex salts have been synthesised in which the SO_4 radical of both the high- and low-sulphate forms is completely replaced by various acid radicals. A list of the compounds that have been prepared is given in *Table I.*

In spite of the fact that silica is the most abundant acidic oxide in Portland cement, no previous attempts have been made to prepare the analogs of the calcium sulphoaluminates which would contain the silicic acid radical SiO_3. This paper is a preliminary report on attempts to synthesise such compounds and also to obtain a replacement of $CaSO_4$ in the high-sulphate calcium sulpho-aluminate by $Ca(OH)_2$.

Preparation of Hydrated Calcium Silicoaluminates.

The silicoaluminate precipitates were made by a modification of a method that has been commonly used in preparing other complex salts of the calcium aluminates. This method consisted in mixing solutions of calcium silicate and aluminate in the desired proportions and adding various amounts of solid calcium oxide.

A 20-litre volume of calcium silicate solution was prepared by boiling purified silica gel with dilute calcium hydroxide solution (0·1 gr. of CaO per litre) for

about 18 hours and removing the undissolved residue by filtration.   The filtrate contained 0·0303 gr. of CaO and 0·387 gr. of SiO_2 per litre.   A quantity of calcium aluminate extract was obtained by shaking 200 gr. of low-sulphate calcium aluminate cement (0·03 per cent. of SO_3) with 4 litres of distilled water for three hours, filtering, and diluting the extract to 12 litres.   The resulting solution contained 0·400 gr. of CaO and 0·581 gr. of Al_2O_3 per litre.

As shown in *Table II*, mixtures of the calcium aluminate and silicate solutions were prepared in which the molar ratios of silica to alumina varied between 1 and 4.   Quantities of solid calcium oxide were then immediately added to the mixtures in amounts sufficient to saturate the solutions with calcium hydroxide (1·15 gr. of CaO per litre) and in addition to provide molar ratios of total lime to alumina ($CaO/Al_2O_3 + CaSiO_3/Al_2O_3$) varying between three and seven in

TABLE II.—PREPARATION OF HYDRATED CALCIUM SILICOALUMINATES.

Experiment number	Composition of mixture			Elapsed time before analysis of samples of precipitate and solution	Molar ratios in precipitate					CaO content of solution
	Calcium aluminate solution [1]	Calcium silicate solution [2]	Solid CaO		Calculated		By analysis			
					$\dfrac{CaO}{Al_2O_3}$	$\dfrac{CaSiO_3}{Al_2O_3}$	$\dfrac{CaO}{Al_2O_3}$	$\dfrac{CaSiO_3}{Al_2O_3}$	$\dfrac{H_2O^3}{Al_2O_3}$	
	ml	ml	g	Days						g/liter
1..........	2,000	1,769	6.04	27	3	1	2.95	1.05	12.3	1.14
2..........	1,000	1,769	3.69	60	1	2	2.00	2.09	12.3	0.53
3..........	1,000	1,769	4.33	59	3	2	3.00	2.05	13.5	1.11
4..........	1,000	1,769	4.65	60	4	2	3.70	2.15	14.8	1.24
5..........	1,000	2,654	5.64	....	3	3	....	....	....	....
6..........	500	1,769	3.47	198	3	4	3.38	4.27	19.2	1.09

[1] Contained 0.581 g of Al_2O_3, 0.400 g of CaO per liter.
[2] Contained 0.387 g of SiO_2, 0.0303 g of CaO per liter.
[3] Determined after washing precipitate with alcohol and ether, and drying to constant weight in a desiccator over calcium chloride.

the precipitates.   The precipitate in experiment No. 1, *Table II*, had the typical silken appearance of suspensions of the hexagonal hydrated calcium aluminates. This characteristic was exhibited in diminishing degree by the precipitates in experiments Nos. 2, 3, and 4, and not at all by those in experiments Nos. 5 and 6. The mixtures, in well-stoppered flasks, were shaken for 15 minutes to disperse the added lime and thereafter at hourly intervals during the first day.   The flasks were stored in the laboratory and subsequently shaken once daily in the course of the first month, after which they were allowed to stand without shaking. Samples of the precipitates were withdrawn at intervals for microscopical examination.

The precipitate from experiment No. 1 became uniform in index of refraction within about one week.   Although very finely divided, it appeared to be entirely composed of very small hexagonal plates, frequently occurring in spherulitic groups.   The crystals are uniaxial negative and have the refractive indexes $\omega = 1·538 \pm 0·003$, $\epsilon = 1·523 \pm 0·003$.   Chemical analyses of the precipitate, after it had stood in contact with solution for 27 days, gave the molar ratios

shown in *Table II*, which correspond to the formula $3CaO.Al_2O_3.CaSiO_3.12H_2O$. The X-ray diffraction pattern of the preparation is similar to those of $3CaO.-Al_2O_3.CaSO_4.12H_2O$ and of $4CaO.Al_2O_3.13H_2O$ (or $3CaO.Al_2O_3.Ca(OH)_2.12H_2O$), with a closer relationship to $4CaO.Al_2O_3.13H_2O$.

In experiment No. 2, the preparation which contained CaO, Al_2O_3, and $CaSiO_3$ in the molar ratios $1:1:2$ took up lime from solution and gave molar ratios of $2:1:2$ in the precipitate. The molar ratios of the other analysed precipitates agreed approximately with the calculated values. All of the preparations listed in *Table II*, except that of experiment No. 1, contained considerable finely-divided or amorphous material as well as hexagonal plate crystal having the optical properties of $3CaO.Al_2O_3.CaSiO_3.12H_2O$. Their X-ray diffrac-

TABLE III.—FORMATION OF NEEDLE CRYSTALS OF CALCIUM SILICOALUMINATE IN PREPARATIONS OF TABLE II AFTER STANDING FOR THREE YEARS IN CONTACT WITH LIME SOLUTIONS.

Experiment number	Approximate molar ratios in precipitate		Approximate proportion of needle crystals in precipitate	CaO in solution
	$\dfrac{CaO}{Al_2O_3}$	$\dfrac{CaSiO_3}{Al_2O_3}$	%	g/liter
1	3	1	20	0.530
2	1	2	30	.344
3	3	2	40	.832
4	4	2	40	.905
5	3	3	40	.663
6	3	4	5	.541

tion patterns corresponded with that of this compound. It was concluded, therefore, that the only silicoaluminate formed in these mixtures is the compound $3CaO.Al_2O_3.CaSiO_3.12H_2O$.

After these determinations, the mixtures were allowed to stand for an additional three years and samples of the precipitates were again withdrawn for microscopical examinations. A new phase was then observed in the precipitates. It appeared usually as long, thin, needle-like prisms. In some preparations where the crystals had a greater width the prisms appeared to possess a hexagonal cross section. They are uniaxial negative, $\omega = 1.487 \pm 0.003$, $\epsilon = 1.479 \pm 0.003$. The crystals have parallel extinction and negative elongation.

Table III shows the approximate proportions of these crystals in the various precipitates. In each precipitate the more abundant phase consisted of the hexagonal plate form of silicoaluminate. No isometric crystals were found, thus indicating the absence of members of the garnet-hydrogarnet series. The needle crystals are believed to be a high-silica calcium silicoaluminate $3CaO.-Al_2O_3.3CaSiO_3.XH_2O$. The habit of these crystals and the measured optical properties, except indexes of refraction, are indentical with those of the high-sulphate calcium sulphoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$. A water content

of 30 to 32 mols. is tentatively assigned to the silicate compound by analogy
with the various similar calcium aluminate complex salts which have been
prepared.

The behaviour of the low-silica form of calcium silicoaluminate in converting
slowly to the high-silica form is entirely similar to the relations exhibited by
the calcium sulphoaluminates. Thus, in the preparation of the high-sulphate
calcium sulphoaluminate, Lerch, Ashton, and Bogue observed that the low-
sulphate compound was usually obtained as an intermediate product, despite
the presence of an excess of $CaSO_4$. The conversion to the more stable sul-
phoaluminate is usually complete in about a week, whereas the corresponding
transformation, in the case of the silicoaluminate compounds, is incomplete
after three years, even in experiment No. 5, where CaO, Al_2O_3, and SiO_2 were
in the proper proportions to form the high-silica product.

TABLE IV.—FORMATION OF NEEDLE CRYSTALS OF CALCIUM SILICOALUMINATE
IN MIXTURES OF CEMENT COMPOUNDS PLACED IN SATURATED LIME SOLUTION
(1·15 CaO PER LITRE) AND ALLOWED TO STAND FOR THREE YEARS.

Experiment number	Mixture [1]	Weight of mixture per volume of lime solution	Approximate proportion of needle form of silicoaluminate in product	CaO in solution
		g/liter	%	g/liter
1	β-2CaO.SiO$_2$+4CaO.Al$_2$O$_3$.Fe$_2$O$_3$	18	10	1.02
2	β-2CaO.SiO$_2$+3CaO.Al$_2$O$_3$	10	30	1.11
3	3CaO.SiO$_2$+4CaO.Al$_2$O$_3$.Fe$_2$O$_3$	10	15	1.08
4	3CaO.SiO$_2$+3CaO.Al$_2$O$_3$	10	0	1.15

[1] The mixtures contained equimolar proportions of the compounds.

The precipitates in experiments Nos. 4 and 5 of *Table III* gave the X-ray
diffraction pattern of $3CaO.Al_2O_3.CaSiO_3.12H_2O$, together with additional lines.
Because of the obscuring effect of the stronger pattern it was not possible to
determine whether these additional lines indicated an X-ray diffraction pattern
similar to that of the high-sulphate calcium sulphoaluminate.

The lime contents of the solutions after three years' contact with the silico-
aluminate precipitates are shown in the last column of *Table III*. These values
indicate that the high-silica calcium silicoaluminate will form in the presence
of solutions containing between 0·3 and 0·9 gr. of CaO per litre.

Formation of High-Silica Calcium Silicoaluminate.

In order to determine if hydrated calcium silicoaluminate will form from
mixtures of the various cement compounds in saturated lime solution, the com-
binations of anhydrous calcium aluminates and silicates shown in *Table IV* were
prepared. The mixtures, which contained the compounds in equimolar pro-
portions, were added to 1-litre portions of saturated lime solution (1·15 gr. of
CaO per litre) and placed in tightly stoppered flasks, which were allowed to stand
for three years with occasional shaking. Samples were then withdrawn for

microscopical examination. As shown in the table, all of the products, except that from the mixture of tricalcium aluminate and tricalcium silicate, contained appreciable amounts of the high-silica calcium silicoaluminate, which appeared as well-developed needle-like prisms. Hexagonal plate crystals were also present in the materials. No attempt was made to identify the crystalline phases which made up the balance of the products. The lime contents of the solutions given in the last column of the table, in conjunction with similar data in *Table III*, indicate that the high-silica silicoaluminate can form in contact with solutions containing calcium hydroxide in amounts between 0·3 gr. of CaO per litre and saturation.

Preparation of Hydrated Hexacalcium Aluminate.

Assarsson has observed the precipitation of needle-shaped hexagonal prisms from extracts of monocalcium aluminate and high-alumina cements. He assigned to this material the formula $5CaO.Al_2O_3.34H_2O$, but stated that it seems to be impossible to prepare the compound without any trace of sulphate. Wells, Clarke, and McMurdie failed to find such an aluminate in the system $CaO-Al_2O_3-H_2O$ at 21 deg. C. and 90 deg. C., and suggested that it may exist in the quaternary system $CaO-Al_2O_3-CaSO_4-H_2O$ as a metastable phase. Bessey expressed the opinion that the compound may be related in structure to the high-sulphate form of calcium sulphoaluminate.

The preparation of such an aluminate was attempted in order to determine if the calcium sulphate in $3CaO.Al_2O_3.3CaSO_4.31H_2O$ can be completely replaced by calcium hydroxide. It was anticipated that the highly basic compound which might result from such replacement would only be stable in contact with solutions containing high concentrations of calcium hydroxide. Accordingly, an excess of calcium oxide was added to 500 ml. of a 10-per cent. sugar solution, the mixture shaken for three hours, and filtered. The filtrate contained 17 gr. of CaO per litre. A calcium aluminate extract was prepared by shaking 50 gr. of calcium aluminate cement (containing 0·03 per cent. of SO_3) with 500 ml. of water for three hours and filtering. This extract contained 1·8 gr. of Al_2O_3 and 1·2 gr. of CaO per litre. The solutions were mixed and allowed to stand. Formation of a precipitate began within a few hours. After five days, samples of the precipitate and solution were withdrawn. Titration of the solution with standard acid showed a lime content of 9·06 gr. of CaO per litre. The sample of precipitate was placed in a flask with 100 ml. of absolute alcohol and the mixture shaken for one hour to remove any sugar from the mother liquor adhering to the particles. The solid material was then filtered off, washed with alcohol and ether, and dried in air overnight.

Microscopical examination showed that the preparation consisted of needle-like prisms entirely similar in appearance to crystals of the high-sulphate form of calcium sulphoaluminate. The crystals are uniaxial negative, $\omega = 1·475 \pm 0·003$ and $\epsilon = 1·466 \pm 0·003$. They have parallel extinction and negative elongation. Analysis of the preparation gave the following composition : CaO, 32·38 per cent. ; Al_2O_3, 9·84 per cent. ; H_2O, 57·46 per cent. ; total, 99·68 per

cent. This corresponds to molar ratios of $5.98CaO : 1Al_2O_3 : 33H_2O$. Accordingly the compound may be assigned the formula $6CaO.Al_2O_3.33H_2O$, or $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$. Its X-ray diffraction pattern is almost indistinguishable from that of $3CaO.Al_2O_3.3CaSO_4.31H_2O$. It is believed that this compound and Assarsson's pentacalcium aluminate hydrate are fundamentally the same, and that the lower CaO/Al_2O_3 ratio of Assarsson's compound is caused by partial hydrolysis.

Although qualitative tests of the $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$ indicated the absence of sulphate, it seemed desirable to prepare it from starting materials in which this constituent was entirely absent. Accordingly a calcium aluminate extract was made from sulphate-free $3CaO.5Al_2O_3$ and added to a lime-sugar solution prepared as before. The resulting crystalline precipitate was identical in all respects with that which resulted from mixing the extract of calcium aluminate cement with lime-sugar solution.

Summary.

Two calcium silicoaluminates, apparently analogs of the high- and low-sulphate forms of calcium sulphoaluminate, were investigated. The low-silica silicoaluminate has the formula $3CaO.Al_2O_3.CaSiO_3.12H_2O$, and occurs as thin hexagonal plates. In contact with lime solutions, it is slowly converted to long needle-like prisms whose habit and optical properties are very similar to those of $3CaO.Al_2O_3.3CaSO_4.31H_2O$. The needle-form of the silicoaluminate has not yet been prepared in a pure state but, by analogy with other similar calcium aluminate complex salts, it has tentatively been assigned the formula $3CaO.Al_2O_3.3CaSiO_3.30-32H_2O$. It was also found in the following mixtures of cement compounds, which had stood in contact with approximately saturated lime solutions for three years : β-$2CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$; β-$2CaO.SiO_2$ and $3CaO.Al_2O_3$; and $3CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$. The role of the silicoaluminates in the setting and hardening of cement warrants further study. The close analogy between the silico- and sulphoaluminates suggests the possible existence of a solid-solution series between these compounds with the formation of sulpho-silicoaluminates, somewhat similar to those reported by Lafuma.

A hexacalcium aluminate hydrate was prepared that appears to be the analog of the high-sulphate form of calcium sulphoaluminate in which calcium sulphate is completely replaced by calcium hydroxide. Its formula may be written $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$. This compound would probably not form as a direct hydration product of Portland cement but might appear, under some conditions, as a solid solution in the high-sulphate form of calcium sulphoaluminate.

Cement Research in Sweden.

FROM funds provided by the Skanska Cement A/B a new Cement and Concrete Institute has been founded, at a cost of £41,000, near the University of Technology of Stockholm. The institute is equipped with an up-to-date laboratory, and has facilities for undertaking indoor and outdoor tests.

Charts for Laboratory Calculations.

A NUMBER of charts for the use of cement and lime chemists are given by Mr. C. J. Knickerbocker in " Rock Products " for February, 1945. The charts are here reproduced, with the following notes by the author.

Slurry Moisture and Fineness.

Fig. 1 is intended to replace the tables used in many laboratories for this purpose. It is rapidly operated and offers a solution comparable in accuracy with that of the balance usually employed for the weighings.

Example.—50 grammes of slurry, when dried, weigh 31·7 grammes.

50 grammes of slurry is sieved and the dried residue weighs 4·3 grammes.

Find the percentage of moisture and dry slurry passing the sieve.

Solution.—2 × (50·0 − 31·7) = 36.6 per cent. moisture.

100 − (2 × 4.3 × 100/100 − 36·6) = 86.4 per cent. passing the sieve.
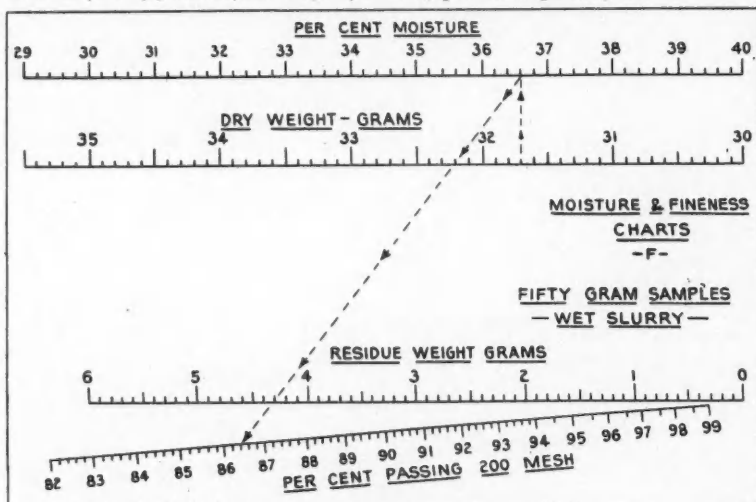
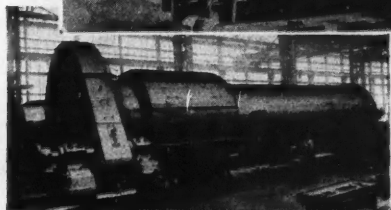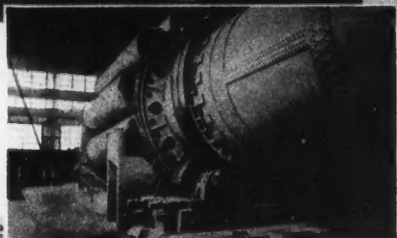**Fig. 1.**

Water Temperature.

It is often desirable to operate combustion calorimeters at a fixed temperature in regard to the room temperature. Fig. 2 allows a rapid approximation to be made of the quantities of cool and warm water required to effect a desired blend.

Example.—2,000 ml. of water at 73·5 deg. are required. Waters of 77 deg. and 69 deg. are available. Ml. cool water = 77·0 − 73·5/77·0 − 69·0 × 2000 = 875 ml. warm water to make balance.

Example (see Fig. 3).—It is desired to cool 77 deg. water with 70 deg. water to make 2,000 ml. that is 73·5 deg. This temperature presumably is low enough to compensate for the warming effect of the bomb assembly and results in firing at the desired temperature. The calculation is similar to the foregoing and, as indicated on the graph, equal amounts are required.

Coal Moisture and Ash.

Fig. 4 is used for converting coal analysis values from the basis of moisture
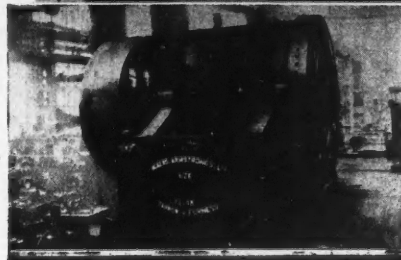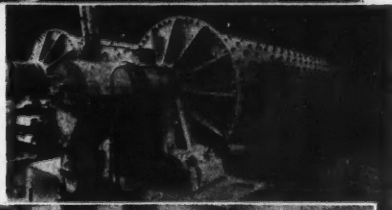
GRAPH FOR APPROXIMATE ADJUSTMENT OF
CALORIMETER WATER TEMPERATURE
-I-

ORIGINAL WATER TEMP.

DEGREES CHANGE

ML. COOLING WATER - 70°

ML. ORIGINAL WATER

NOTE - PROPORTION WATERS IN
2 LITER CYLINDER.
MAKE FINAL ADJUSTMENT IN
2000 ML. VOL. FLASK.
FIRING TEMP. TO BE ONE DEGREE
BELOW JACKET TEMP.

Fig. 3.

WATER TEMPERATURE ADJUSTMENT GRAPH
-II-

SUBSTITUTE FOLLOWING
TERMS IN:

$$ML. B = \frac{X-A}{X-B} \cdot 2000$$

B = COOL WATER TEMPERATURE
X = WARM WATER TEMPERATURE
A = DESIRED MIXTURE

LOCATE VOLUME RATIOS
ON DIAGONAL AT LEFT

ML. B - COOL -

ML. X - WARM

X-B

X - DEGREES

LOCATE X-A & X-B
VALUES HERE

X-A & X-B

A & B DEGREES

X-A
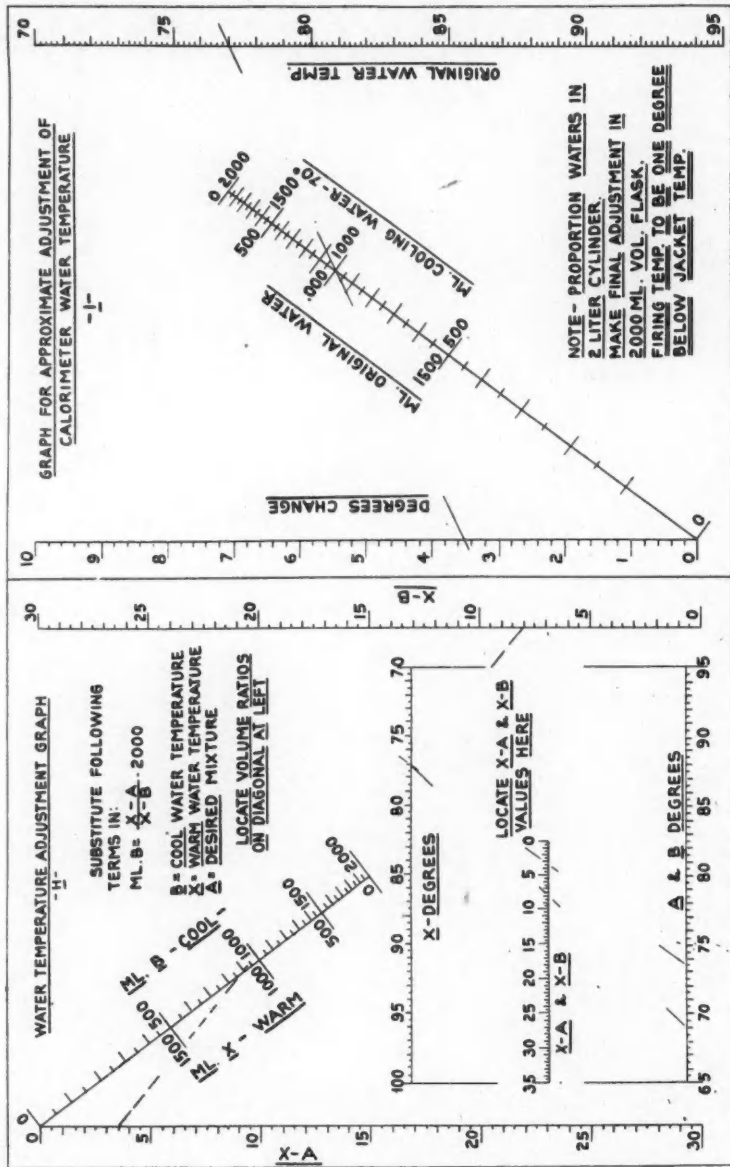
Fig. 2.
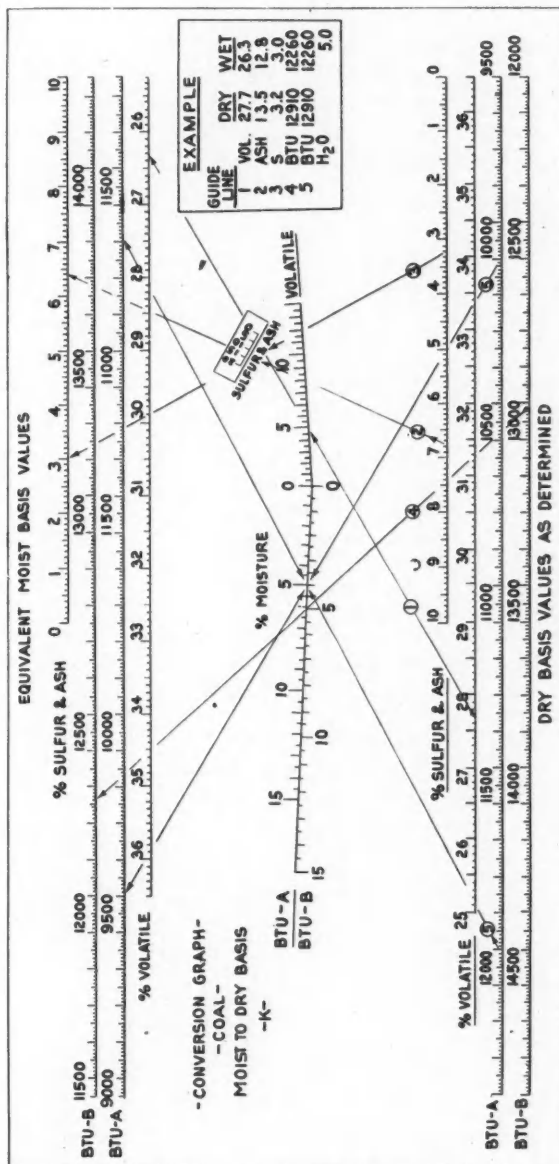
Fig. 4.

content of the analysed sample to that of the moist basis as received.   A similar
graph converts to an ash-free basis.   As shown, one alignment suffices for each
operation.   The original size being 9 in. by 19 in., the calculations may be carried
to an extent exceeding the accuracy of reading the usual coal calorimeter ther-
mometer in terms of corresponding B.T.U. content.   The diagonals corresponding
to the base line used are intersected at the moisture content corresponding to
the difference between the analysed coal moisture content and the moisture
content of the coal as received at the scales.   It is assumed that corrections
have been made for free or combined moisture in the analysed sample.

X-Ray Analysis in Industry.

THE X-ray Analysis Group of the Institute of Physics held its annual conference
in London on April 12 and 13.   The proceedings included a symposium on the
equipment of X-ray laboratories, at which Dr. R. F. Hanstock dwelt on equip-
ment for determining residual stresses in metals ; Mr. H. S. Peiser described types
of X-ray apparatus, and Dr. W. A. Wooster described accessory crystallographic
equipment.   Professor J. D. Bernal gave a talk on the future of X-ray analysis.
Among those who took part in a discussion on the application of optical principles
to the interpretation of X-ray diffraction were Professor Sir Lawrence Bragg,
Dr. H. Lipson, Mr. G. B. Hey, and Professor J. M. Robertson.